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Potential for Recovery of Rutile and Other Byproducts From Western Copper Tailings

By E. G. Davis, G. V. Sullivan, and W. E. Lamont

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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNITED STATES DEPARTMENT OF THE INTERIOR
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

gr	grain	mt	metric ton
g	gram	mt/d	metric ton per day
g/L	gram per liter	pct	percent
h	hour	lb	pound
L	liter	lb/st	pound per short ton
µm	micrometer	s	second
mL	milliliter	st	short ton
min	minute	wt pct	weight percent

POTENTIAL FOR RECOVERY OF RUTILE AND OTHER BYPRODUCTS FROM WESTERN COPPER TAILINGS

By E. G. Davis[1], G. V. Sullivan[2], and W. E. Lamont[3]

ABSTRACT

The Bureau of Mines studied tailings samples from 11 large-scale western copper operations to determine the potential for recovery of rutile and other critical and strategic minerals. Up to 15 pounds per short ton (lb/st) TiO_2 was found in these samples; however, only 9 to 44 pct of the TiO_2 was liberated rutile. For one sample, gravity preconcentration, grinding, and flotation recovered 34 pct of the TiO_2 in a 54.8-pct-TiO_2 concentrate. Over 0.38 lb/st W was found in some of the tailings samples. Scheelite was identified as the major W mineral. Nine of the eleven samples contained about 0.02 to 0.18 lb/st Co. Pyrite was the principal Co-bearing sulfide mineral, with Co contained in about one-fifth of the pyrite grains. Up to 30 pct of the Co was concentrated in a bulk sulfide flotation concentrate.

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INTRODUCTION

Two of the goals of the Bureau of Mines are to maximize mineral recovery from domestic resources and to conserve mineral resources. To help meet these goals, the Bureau has been investigating the recovery of valuable minerals from mineral processing tailings. One of the areas under study has been the recovery of rutile from western Cu mill tailings (1).[4] Rutile (TiO_2) and ilmenite ($FeTiO_3$) are the two major Ti-bearing minerals utilized in the production of Ti metal and TiO_2 pigment. Rutile used domestically is imported at the rate of 170,000 st annually (2). In 1953, a survey by the U.S. Geological Survey (3) indicated that most of the western Cu deposits being mined at that time contained from 6 to 15 lb/st TiO_2. The TiO_2 is present as rutile, anatase, ilmenite, and other Ti minerals. One such operation--San Manuel, a division of Magma Copper Co., a wholly owned subsidiary of Newmont Corp.--had ore reserves of nearly 1 billion st. In addition to 15 lb/st Cu, this reserve also contains 15 lb/st TiO_2 (4-6). More recently, Force (7) recorded the origin and mode of occurrence of rutile in porphyry ore. He estimated the potential byproduct rutile resource in the active western copper mines to be in excess of 5 million mt, with a potential rutile recovery rate of 300 mt/d. Sullivan and Llewellyn (8) estimated that recovery of rutile from two of the tailings they investigated would amount to about 32 pct of 1980 U.S. imports.

A rutile flotation technique for rutile-bearing Cu mill tailings was developed by Llewellyn and Sullivan (1). The success of that investigation led to this research, which sought to determine the feasibility of rutile recovery from other western copper mines.

Eleven companies, some of which wished to remain anonymous, cooperated in this study, submitting a total of 15 flotation plant tailings samples and one leach plant waste product. Daily capacity of these 11 operations is substantially over 500,000 st (9). Consequently, recovery of rutile and/or other potentially valuable minerals in these plant waste materials could represent very significant tonnages.

DESCRIPTION OF SAMPLES

Samples of Cu mill tailings were requested from all major western copper producers so that the elements in their waste products could be inventoried. Most of the operating companies provided several barrels of tailings. However, at the time, the copper market was in a depressed state, so some of the properties were not operating. Several of these companies furnished samples of drill-hole composites of old tailings ponds or composites of monthly operating samples taken from storage.

Each sample was thoroughly mixed or slurried before a representative sample was taken for head analyses, sizing, and sink-float studies.

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

CHEMICAL ANALYSES

Representative samples of each waste tailings were analyzed by wet chemical means for several major elements and some of the minor elements such as Ti, Cu, Fe, and S. Trace elements were analyzed by neutron activation[5] and X-ray fluorescence. The resulting analyses (table 1) indicated that the TiO_2 content in the tailings products varied from 3.2 to 15 lb/st. The tailings also contained varying amounts of Cu that were not recovered in the original processing of the ore and trace amounts of Mo, W, Co, V, Zn, and Ni. The recovery of some of these elements may be of interest especially if they can be recovered in addition to the TiO_2.

PHYSICAL ANALYSES

X-ray Diffraction

Representative samples of each waste tailings were analyzed using X-ray diffraction to determine the mineralogical composition of each sample. Results of the diffraction studies (table 2) indicated that the quartz was a major constitutent in 15 of the samples. Garnet, orthoclase, plagioclase, and mica were reported in minor to major amounts. The concentration of rutile was too low in the bulk tailings for detection using X-ray diffraction.

Sizing Studies

The samples were wet sieved at 150 and 37 μm and sedimentation sized at 10 μm. The sized fractions from each sample were analyzed for TiO_2 and Cu to determine the size distribution of the TiO_2 and Cu minerals. Results of this study are summarized in table 3. In some of the samples, the Cu concentrated slightly in the plus 150-μm size fraction, probably as a result of not achieving liberation of the copper sulfide minerals during grinding. In most of the samples, the Cu also concentrated slightly in the minus 10-μm fraction, possibly resulting from (1) ineffective flotation of fine copper sulfide in the original flotation process or (2) the presence of oxide Cu in the fine sizes. The TiO_2 concentrated slightly in the minus 37- plus 10-μm fraction.

Sink-Float Studies

The plus 10-μm size fraction was sink-float separated at specific gravities of 2.93 and 3.3 using heavy liquids. Each specific gravity (sp gr) fraction was analyzed for TiO_2 to determine its liberation characteristics. The liberated Ti minerals were concentrated in the sink 3.3 sp gr product, and the partially liberated Ti minerals were concentrated in

[5]The neutron activation was done in the University of Utah's TRIGA reactor, which operates with a flux density of 10^{12} neutrons per square centimeter per second. The tests were performed on 1-g samples that were heat sealed in plastic capsules and irradiated for either 15 s or 10 min, depending on the amount of contained elements, their half lives, and their neutron-absorption cross sections. Flux monitors were Au for samples irradiated for 15 s and Fe for samples irradiated for 10 min. Counting was done with a Ge-Li detector coupled to a 4,096-channel analyzer.

TABLE 1. - Analyses of western Cu tailings sample, pounds per short ton

Sample[1]	Wet Analyses								X-ray fluorescence							Neutron activation				
	TiO_2	Cu	Al_2O_3	CaO	K_2O	MgO	Na_2O	SiO_2	Fe	S	Ni	P	U	V	Zn	As	Co	Mn	Mo	W
1A.....	15	2.8	300	24	98	20	32	1,316	44	58	0.30	1.22	0.02	1.0	0.09	0.01	0.02	0.12	N	0.11
1B.....	14.6	1.4	290	36	90	32	38	1,336	44	18	NA	NA	NA	NA	NA	N	.10	N	N	.04
2.....	10.8	1.7	262	8	92	18.4	8	1,385	50	138	.22	.87	.02	1.0	.13	.02	.02	.22	0.24	.04
3.....	8	1.7	302	44	103	20	52	1,312	44	98	.18	1.0	.02	.06	.18	N	.11	.62	.11	.03
4.....	7.4	4.6	298	32	80	28	18.8	1,295	70	78	.25	.67	.03	.99	.65	N	N	.70	.08	.02
5.....	4.2	2.9	82	522	7	38	3.2	674	312	100	NA	NA	NA	NA	NA	.03	.09	6.4	.27	.05
6.....	8.6	1.7	224	72	94	48	26	1,290	54	78	NA	NA	NA	NA	NA	.02	.10	.92	.06	.23
7A.....	5.4	5.9	105	286	32	134	10	964	152	76	NA	NA	NA	NA	NA	.06	N	3.4	1.1	.29
7B.....	3.2	1.9	110	348	34	64	8.6	952	184	96	.34	1.03	.03	1.0	1.27	.03	.18	1.5	.15	.36
7C.....	8.8	1.4	174	280	50	126	11.2	1,012	96	40	NA	NA	NA	NA	NA	N	.10	N	N	.38
8.....	6.8	1.6	162	78	60	62	14	1,432	36	74	.22	.7	.02	.99	.17	.02	.17	.79	.09	.08
9A.....	8.4	1.6	252	16	126	9.4	10.8	1,452	36	74	.23	.67	.02	.99	.37	N	.08	.19	N	N
9B.....	11.6	1.5	248	9	126	9.2	10.6	1,434	26	84	NA	NA	NA	NA	NA	.03	.10	.13	N	.04
9C.....	8.6	1.4	256	10	124	9.2	16	1,474	26	12	NA	NA	NA	NA	NA	N	.10	N	N	.01
10.....	10.6	1.7	224	52	106	58	19.2	1,352	54	44	NA	NA	NA	NA	NA	.09	.11	.34	.08	.06
11.....	8.2	2.4	316	5	130	14	11.8	1,334	28	40	.28	.38	.02	.99	.12	.01	.03	.19	.05	.03

N Not detected. NA Not analyzed. [1]Letters designate separate samples from the same copper operation or company.

TABLES 2. - X-ray diffraction studies of tailings samples

Sample	Quartz	Orthoclase	Plagioclase	Mica	Pyrite	Other
1A....	Major...	Minor.....	Minor.....	Minor...	Trace...	Trace: kaolinite.
1B....	..do....	..do.....	..do.....	..do....	..do....	Do.
2.....	..do....	..do.....	Trace.....	..do....	Minor...	Do.
3.....	..do....	Minor to major.	Minor to major.	ND.....	ND.....	Minor: kaolinite.
4.....	..do....	Minor.....	Minor.....	..do....	Minor...	Do.
5.....	Minor...	ND.....	ND.....	ND.....	ND.....	Major: garnet; minor: diopside.
6.....	Major...	Minor.....	Minor.....	Minor...	Trace to minor.	Trace: chlorite, calcite, amphibole.
7A....	..do....	ND.....	Trace.....	Trace...	ND.....	Trace: chlorite; minor: amphibole, diopside.
7B....	..do....	Minor.....	..do.....	..do....	Trace...	Minor to major: garnet; minor: calcite; trace: amphibole.
7C....	..do....	..do.....	..do.....	Trace to minor.	..do....	Minor to major: calcite; trace: amphibole, garnet.
8.....	..do....	..do.....	..do.....	..do....	..do....	Trace: diopside, amphibole, kaolinite.
9A....	..do....	Minor to major.	..do.....	Minor...	ND.....	ND.
9B....	..do....	Major.....	ND.....	..do....	Trace...	ND.
9C....	..do....	..do.....	Trace.....	Trace...	..do....	Minor to major: garnet; minor: calcite; trace: amphibole.
10....	..do....	Minor.....	..do.....	Minor to major.	..do....	ND.
11....	..do....	Minor to major.	..do.....	..do....	N.....	Trace: hematite, kaolinite.

N Not detected. ND Not determined.

the fraction between 2.93 and 3.3 sp gr. As shown in table 4, the three samples containing the smallest amount of TiO_2 also contained large quantities of garnet which reported to the highest specific gravity fraction of 3.3. In the other samples, between 9 and 44 pct of the TiO_2 was in the sink 3.3 sp gr fraction. For sample 1B, the size analysis of the sink 3.3 sp gr fraction showed that 82 pct of the TiO_2 in that high-density fraction was between 75 and 10 μm in size. Although the liberation size for the Ti minerals was smaller than many of the tailings particles, several of the tailings contained sufficient liberated TiO_2 to be potentially viable resources. As shown in table 5, half of the tailings samples contained more than 2 lb/st liberated TiO_2. The analyses for five other potentially valuable elements found in the sink 3.3 sp gr fraction are also shown in table 5.

TABLE 3. - TiO_2 and Cu analyses of sized tailings fractions

Sample	Analysis, lb/st		Wt pct	Analysis, lb/st		Distribution, pct		Wt pct	Analysis, lb/st		Distribution, pct	
	TiO_2	Cu		TiO_2	Cu	TiO_2	Cu		TiO_2	Cu	TiO_2	Cu
	Composite		Plus 150 μm					Minus 150 plus 35 μm				
1A.....	15.4	2.8	17.6	12.6	4.68	14.5	29.7	36.2	13.8	1.48	32.6	19.6
1B.....	14.6	1.4	29.9	9.2	2.18	18.5	45.6	34.6	12.0	.92	27.9	22.3
2[1].....	10.8	1.7	56.6	9.2	.60	43.1	42.5	18.8	15.4	.48	27.4	12.5
3.....	8.0	1.7	40.5	8.0	1.70	36.1	41.0	31.2	9.6	.50	33.4	9.6
4.....	7.4	4.6	35.9	6.6	4.02	32.2	35.7	24.1	8.2	2.66	27.1	15.8
5.....	4.2	2.9	13.6	4.0	3.18	13.0	15.8	43.2	3.6	1.60	37.5	26.3
6.....	8.6	1.7	40.9	8.8	2.42	40.0	63.6	26.8	7.8	1.10	23.3	19.5
7A.....	5.4	5.9	22.7	4.8	5.54	20.9	20.7	35.8	4.8	5.10	33.0	29.8
7B.....	3.2	1.9	16.2	3.0	3.50	15.4	16.8	43.2	2.6	1.56	35.9	20.3
7C.....	8.8	1.4	12.7	5.0	2.60	12.9	27.2	33.1	3.8	1.12	25.7	29.9
8.....	6.8	1.6	28.3	6.0	1.74	26.9	32.9	37.1	5.2	1.12	30.4	27.6
9A.....	8.4	1.6	38.2	5.6	2.06	24.2	52.0	37.5	9.6	.88	34.5	18.7
9B.....	11.6	1.5	34.4	8.4	1.00	26.2	25.7	32.0	10.6	1.10	30.9	25.7
9C.....	8.6	1.4	42.3	4.6	ND	28.9	ND	24.3	7.0	ND	25.3	ND
10.....	10.6	1.7	19.9	8.4	2.36	16.6	32.4	43.8	8.4	.78	36.2	23.9
11.....	8.2	2.4	28.9	5.8	1.66	20.1	22.7	35.8	8.2	.78	34.7	13.2
	Head		Minus 35 plus 10 μm					Minus 10 μm				
1A.....	15.4	2.76	17.4	26.0	1.42	29.5	8.7	28.8	12.4	4.02	23.4	42.0
1B.....	14.8	1.44	18.8	30.0	.66	37.9	8.7	16.7	14.0	2.0	15.7	23.4
2[1].....	12.0	.80	5.9	26.0	.62	12.2	5.0	18.7	10.8	1.74	16.7	40.0
3.....	9.0	1.66	12.2	12.6	.62	17.1	4.8	16.1	7.4	4.6	13.4	44.6
4.....	7.4	4.04	9.1	12.4	2.56	15.3	5.9	30.9	6.0	5.54	25.4	42.6
5.....	4.2	2.66	21.5	4.4	2.00	22.6	16.5	21.7	5.2	5.10	26.9	41.4
6.....	9.0	1.54	14.6	10.0	.72	16.2	6.5	17.7	10.4	.94	20.5	10.4
7A.....	5.2	6.10	22.0	6.4	.24	27.1	19.0	19.5	5.0	9.56	19.0	30.5
7B.....	3.2	3.34	23.5	3.8	1.94	28.8	13.8	17.1	3.6	9.58	19.9	49.1
7C.....	4.8	1.24	23.7	5.0	.58	25.1	11.5	29.5	6.0	1.32	36.3	31.4
8.....	6.4	1.52	17.1	7.0	1.00	19.0	11.9	17.5	8.6	2.44	23.7	27.6
9A.....	8.8	1.50	14.5	16.8	.80	27.7	8.0	15.8	7.6	2.02	13.6	21.3
9B.....	11.0	1.40	14.9	18.6	1.30	25.3	14.3	18.7	10.4	2.56	17.6	34.3
9C.....	6.8	ND	21.4	12.0	ND	37.4	ND	11.5	5.0	ND	8.4	ND
10.....	10.2	1.50	18.7	16.0	.94	29.5	12.7	17.6	10.2	2.48	17.7	31.0
11.....	8.4	2.12	16.9	13.8	1.16	28.0	9.4	18.9	7.6	6.16	17.2	54.7

ND Not determined.

[1]Sample 2 contained significant quantities of water-soluble Cu (determined by analysis of supernatant water). Repeat analyses were all within 0.002 pct Cu of the original analysis.

TABLE 4. - Distribution of TiO_2 in sink-float fractions of the plus 10-μm tailings samples

Sample	Analysis, lb/st TiO_2	Wt pct	Analysis, lb/st TiO_2	Distribution, pct TiO_2	Wt pct	Analysis, lb/st TiO_2	Distribution, pct TiO_2
	Head	Float 2.93 sp gr			Sink 2.93 sp gr float 3.3 sp gr		
1A....	15.0	68.6	7.0	31.3	0.7	124	5.7
1B....	14.6	80.0	7.9	43.0	1.2	94	7.7
2.....	10.8	75.7	5.2	32.0	1.1	120	11.2
3.....	8.0	79.3	4.4	37.4	2.3	84	20.5
4.....	7.4	62.7	5.2	42.9	1.8	36	8.4
5.....	4.2	15.6	3.4	12.2	6.7	5	8.3
6.....	8.6	75.8	7.4	65.6	2.5	14	4.2
7A....	5.4	44.2	5.2	36.5	20.1	6	19.5
7B....	3.2	37.4	2.2	23.9	9.3	4.6	11.8
7C....	8.8	44.8	3.8	37.2	11.8	4.4	11.4
8.....	6.8	75.6	4.8	58.2	5.1	7.6	6.2
9A....	8.4	82.6	4.0	35.0	.5	146	8.0
9B....	11.6	78.2	9.6	58.7	1.4	66	7.3
9C....	8.6	86.5	3.8	48.0	.6	80	7.5
10....	10.6	76.3	8.6	57.8	3.0	26	7.0
11....	8.2	76.2	5.4	50.3	4.2	24	12.6
	Composite	Sink 3.3 sp gr			Minus 10 μm		
1A....	15.3	1.9	320	39.7	28.8	12.4	23.3
1B....	14.8	2.1	234	33.4	16.7	14.0	15.9
2.....	12.0	4.5	98	37.6	18.7	10.8	17.2
3.....	9.0	2.3	122	29.5	16.1	7.4	12.6
4.....	7.4	[1]4.6	40	24.2	30.9	6.0	24.5
5.....	4.2	56.0	4.0	51.7	21.7	5.2	27.2
6.....	9.0	4.0	9.2	8.8	17.7	10.4	21.4
7A....	5.2	[1]16.2	11.6	26.7	19.5	5.0	16.0
7B....	3.2	[1]36.2	4.6	47.3	17.1	3.6	17.4
7C....	4.8	13.8	6.4	19.7	29.5	4.8	29.5
8.....	6.4	1.8	38	11.0	17.5	8.6	24.4
9A....	8.8	1.7	238	43.9	15.8	7.6	13.1
9B....	11.0	1.7	138	18.6	18.7	10.4	15.4
9C....	6.8	1.4	184	36.1	11.5	5.0	8.4
10....	10.2	3.1	70	19.4	17.6	10.2	16.0
11....	8.4	.7	222	19.5	18.9	7.6	17.2

[1]Sample contained large quantity of garnet.

TABLE 5. - Analyses for selected elements in sink 3.3 sp gr fractions of tailings samples

Sample	Wt pct[1]	Analysis, lb/st						TiO_2 in tailings, lb/st
		TiO_2	Cu	Mo	Sn	W	Zr	
1A....	1.9	320	10.2	1.6	0.16	0.8	5.0	6.08
1B[2]...	2.1	216	1.0	ND	ND	.44	ND	4.54
2.....	4.5	98	3.0	5.2	.16	1.12	3.2	4.41
3.....	2.3	122	4.8	2.2	.18	.96	2.8	2.81
4.....	4.6	40	19.8	6.8	.32	.8	1.4	1.84
5.....	4.5	1.8	11.4	2.2	.12	.8	.2	.08
6.....	4.0	19.2	6.8	2.0	.10	1.12	.8	.77
7A....	4.0	5.6	15.6	2.6	.12	1.74	2.0	.22
7B....	2.9	4.6	4.8	2.4	.12	4.12	1.0	.13
7C[3]...	13.8	6.4	1.8	ND	ND	.88	ND	.88
8.....	1.8	38	10.2	2.8	.12	3.18	1.6	.68
9A....	1.7	238	23.4	9.0	.38	.64	5.4	4.05
9B....	1.7	138	26.4	4.8	.14	.64	3.0	2.35
9C[4]...	1.4	184	44.0	ND	ND	.64	ND	2.58
10....	3.1	70	9.8	2.2	.18	.8	2.2	2.17
11....	.7	224	23.6	5.0	.16	1.12	1.0	1.57

ND Not determined.

[1]Weight percent of 3.3 sp gr sink fractions in tailings. Garnet was removed from 3.3 sp gr sink fraction of samples 5, 7A, and 7B.

[2]Analyzed 1.02 lb/st Co.

[3]Analyzed 0.12 lb/st Co.

[4]Analyzed 0.48 lb/st Co.

Mineralogical Examination of High-Density Fractions

The Bureau analyzed samples of minus 150-, plus 37-µm, high-density fractions to determine their mineralogical contents. Several representative fractions were prepared from each of the samples. One set was cast in methyl methacrylate buttons which were then briquetted in lucite. They were later polished and examined using a reflected-light polarizing microscope. Another set was examined in oils using a transmitted-light polarizing microscope. Finally, a third set was pulverized and analyzed with an X-ray powder diffractometer.

Table 6 presents the combined results of the three separate mineral examinations. No effort was made to quantify the mineral species because of the large size difference between the minus 150- and plus 37-µm fractions. The presence of an unidentified oxide mineral was noted in several of the samples; further examinations and chemical analyses did not identify this mineral.

Microprobe Analyses of Two High-Density Fractions

The sink fractions of samples 1A and 9A were examined by electron beam microprobe to determine the amount and mode of occurrence of the TiO_2 minerals. The approximate mineral contents of the high-density sink fractions were estimated as follows, in percent:

Mineral	Sample 1A	Sample 9A
Pyrite.....	60	60
Ti minerals.....	25	20
Zircon.....	5	5
Fe minerals.....	5	10
Miscellaneous.....	5	5

TABLE 6. - Mineralogical identification of minus 150- plus 37-μm high-density fractions

Mineral	Sample														
	1A	1B	2	3	4	5	6	7A	7B	7C	8	9A	9B	9C	10
Pyrite.....	M	M	M	M	M	M	C	M	M	M	M	M	M	M	M
Azurite.....	N	N	N	N	T	N	N	N	N	N	N	N	N	N	N
Beryl.....	N	N	N	m	N	N	N	N	N	N	N	O	N	N	m
Bornite.....	N	N	N	N	T	T	T	N	N	N	N	N	N	N	N
Chalcopyrite..	m	T	O	O	O	O	C	O	O	m	O	m	O	C	O
Corundum.....	N	N	N	N	N	T	N	N	N	N	N	N	N	N	N
Covellite.....	T	T	O	T	O	N	O	T	N	T	T	O	m	O	N
Cuprite.....	m	T	m	m	m	m	m	m	m	m	m	m	m	m	T
Galena.....	N	N	N	N	N	N	N	N	N	N	N	T	N	N	N
Garnet.....	N	N	N	N	m	m	m	m	O	N	C	N	N	N	C
Hematite.....	N	N	N	N	m	N	C	m	C	C	m	m	N	N	N
Magnetite.....	m	N	m	m	m	m	M	C	C	N	m	m	C	N	m
Malahite.....	N	N	N	N	T	N	N	N	N	N	T	N	N	N	N
Marcasite.....	N	N	N	N	N	T	N	N	N	N	N	N	N	N	T
Molybdenite...	N	N	N	N	N	N	N	N	N	N	N	O	N	N	T
Monazite.....	N	N	N	N	N	N	N	N	N	N	N	N	m	m	O
Pyrrhotite....	T	T	N	N	N	N	N	N	N	N	N	N	N	N	N
Rutile.....	C	C	m	C	O	T	T	T	T	T	O	C	m	T	O
Sphalerite....	T	T	N	N	N	T	T	N	N	N	N	O	N	N	N
Sphene.....	N	N	N	N	m	N	N	N	N	N	N	N	N	N	N
Zircon.....	m	N	m	m	O	N	O	O	O	N	m	m	O	N	O

C Common (>10 to <50 pct). N Not detected.
M Major (>50 pct). O Occasional (<1 pct).
m Minor (>1 to <10 pct). T Trace (1 or 2 gr).

NOTE.--Sample 11 was not analyzed.

The miscellaneous minerals included chalcopyrite, covellite, xenotime, molybdenite, barite, galena, sphalerite, and other silicates and oxides. The modes of occurrence and associations of the Ti-bearing minerals were as follows, with content shown in percent:

Mineral	Sample 1A	Sample 9A
Free rutile.....	65	65
Rutile with silicate intergrowth.....	30	10
Ilmenite.....	5	15
Complex composite...	1	10

The rutile with silicate intergrowth, which was common in sample 1A, is shown in figure 1. Figure 1*A*, a negative electron current image, shows the rutile as light gray and the silicate as dark gray. Figures 1*B* and 1*C* show the distributions of Ti and Si, respectively.

The complex composite common in sample 9A is shown in figure 2. Figure 2*A* is a negative electron current image, and figures 2*B*, 2*C* and 2*D* are the elemental distributions of Ti, Fe, and Al, respectively. In figure 2*A*, the rutile appears as dark gray, and the large, porous mineral grain consists of a composite of ilmenite, FeO_2, and aluminium silicate. About 10 pct of the Ti appears to be tied up in this manner.

BENEFICIATION

Beneficiation studies were conducted to further define the chemical and physical natures of the critical and strategic minerals in the tailings and to determine the feasibility of several beneficiation schemes for recovering these minerals. Virtually all of the beneficiation studies were conducted on sample 1B from the San Manuel operation. This sample contained 14.6 lb/st TiO_2, mostly as rutile, 1.4 lb/st Cu, and 0.1 lb/st Co.

RUTILE RECOVERY

Llewellyn and Sullivan devised a flotation method for recovering the rutile from San Manuel Cu tailings (8). First, the as-received tailings were deslimed at 10 μm. After adjusting the pH to 9.8 with Na_2Co_3, the sulfide minerals were floated using sodium ethyl xanthate as the collector. Then the carbonaceous minerals were floated at pH 9.8 using sodium oleate as the collector and dextrin as a rutile depressant. After thickening to remove most of the high-pH water, H_2SO_4 was used to lower the pH to 2.4 followed by rutile flotation using petroleum sulfonate as the collector and HF as a silicate depressant. Both the sulfide and carbonate flotations significantly lowered the acid consumption required to maintain the 2.4 pH for rutile flotation. After three cleaning flotation stages, the rutile concentrate contained 34.7 pct TiO_2, and the method recovered 31 pct of the TiO_2. Size analysis of the rutile concentrate showed that only the minus 75-μm rutile was recovered. Grinding the original tailings through 75 μm increased the TiO_2 recovery to 34 pct. However, the grinding costs for these tailings would greatly exceed the benefit of the increased rutile recovery.

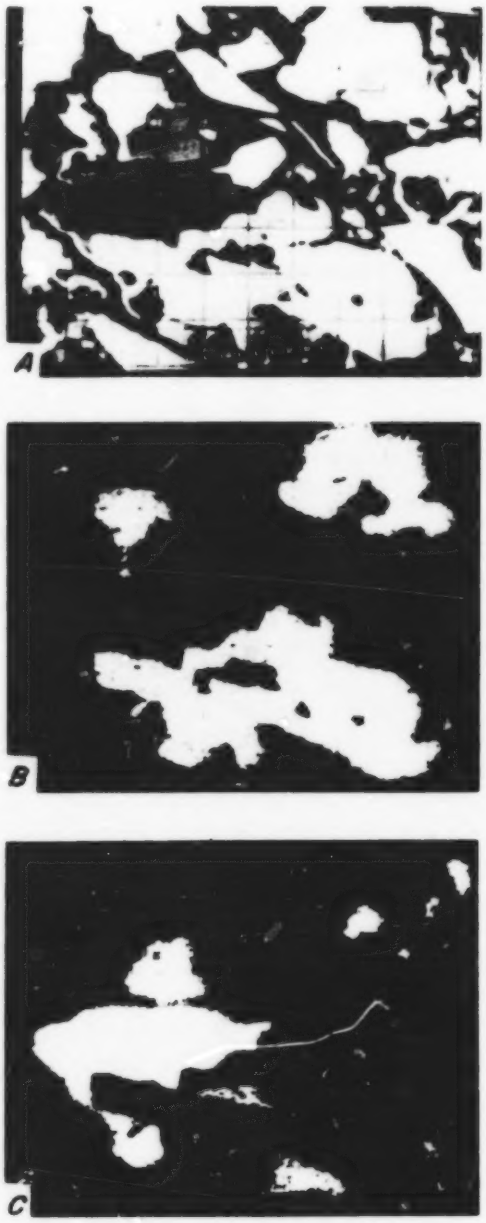

FIGURE 1.—Electron microprobe photographs of high-density fraction of sample 1A (X 200). *A*, Negative electron current image; *B*, Ti distribution; *C*, Si distribution.

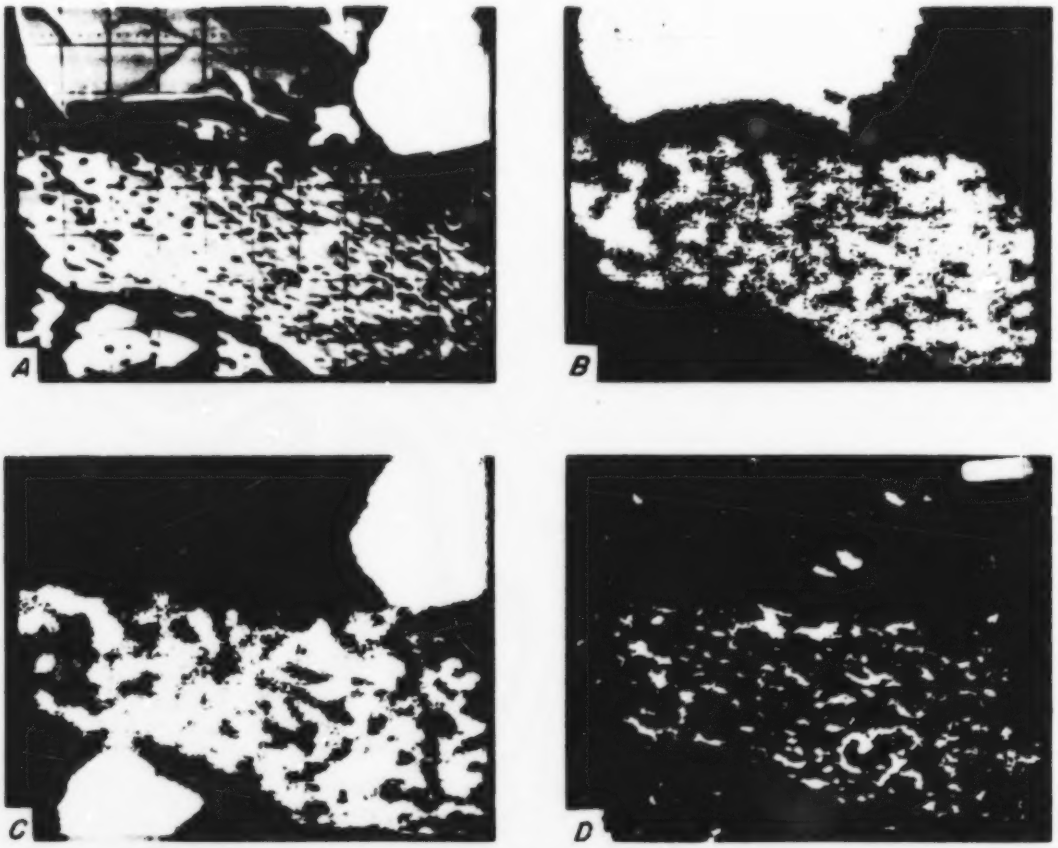

FIGURE 2.—Electron microprobe photographs of high-density fraction of sample 9A (X 200). *A*, Negative electron current image; *B*, Ti distribution; *C*, Fe distribution; *D*, Al distribution.

Sizing and Flotation

Llewellyn and Sullivan pointed out that preconcentration of the plus 75-µm rutile might prove to be an economical alternative to bulk grinding for increased rutile recovery. Building upon their research, three additional beneficiation schemes were studied.

The first alternate method classified the tailings at 75 µm and discarded the plus 75-µm material. A flow diagram of this method is shown in figure 3. The minus 75-µm material was treated according to the method devised by Llewellyn and Sullivan, except for the substitution of an anionic sulphosuccinate for the petroleum sulfonate in the rutile flotation. About 30 pct of the TiO_2 was recovered in a 55.7-pct-TiO_2 concentrate. Heavy-liquid analysis of the rutile flotation tailings indicated that 87 pct of the liberated rutile was recovered in the rutile concentrate. A summary of the TiO_2 distribution is shown in table 7. Nearly all of the TiO_2 lost in the flotation tailings was in the form of small grains locked with silicate minerals.

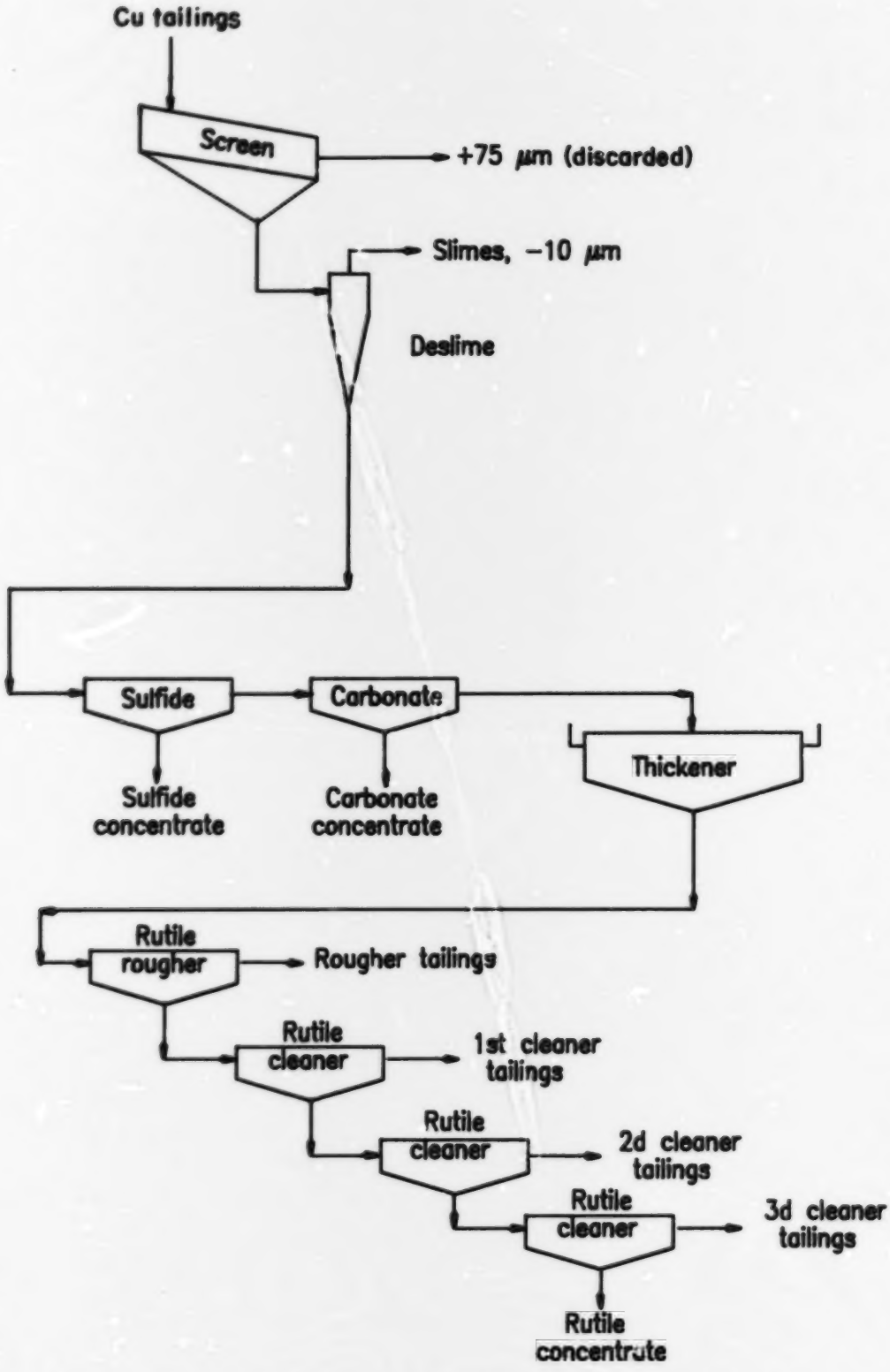

FIGURE 3.—Flow diagram, first alternate to Llewellyn and Sullivan method for rutile recovery.

TABLE 7. - Results of sulfide, carbonate, and rutile flotation

(2 1,000-g charges)

Product	Flotation feed, wt pct	Complete sample, wt pct	TiO_2, pct			
			Analysis		Distribution	
			Flotation feed	Complete sample	Flotation feed	Complete sample
Rutile cleaner concentrate.....	1.1	0.4	55.70	55.70	54.3	[1]29.5
Sulfide cleaner concentrate.....	4.4	1.5	.45	.45	1.8	.9
Carbonate cleaner concentrate.....	4.9	1.7	.86	.86	3.7	1.9
Combined rutile cleaner tailing.....	2.3	.8	2.36	5.4	5.4	2.8
Rutile rougher tailing.....	87.3	30.6	.45	.45	34.8	18.2
Plus 200-mesh material.....	NAp	48.3	NAp	.49	NAp	31.2
Minus 10-μm slimes...	NAp	16.7	NAp	.70	NAp	15.5
Composite.....	100.0	100.0	1.13	.744	100.0	100.0

NAp Not applicable. [1]83 pct of available TiO_2.

Preconcentration and Flotation

The second alternate method employed gravity preconcentration on the plus 75-μm portion of the tailings. Figure 4 shows the flow diagram for this method. Using a concentrating table, the plus 150-μm fraction and minus 150- plus 75-μm fraction were independently treated to form a heavy-mineral concentrate containing 17 pct of the plus 75-μm TiO_2 and rejecting over 96 pct of the gangue. Heavy-liquid analysis showed that 69 pct of the plus 75-μm liberated rutile was recovered in the table concentrate. After combining the gravity concentrate with the minus 75-μm material, the modified Llewellyn and Sullivan flotation method (anionic sulphosuccinate substituted for the petroleum sulfonate) produced a 30.2-pct-TiO_2 concentrate, but recovered only 24 pct of the TiO_2.

Preconcentration, Grinding, and Flotation

The third alternate method employed gravity preconcentration followed by grinding. As shown in figure 5, the plus 150-μm fraction and the minus 150- plus 75-μm fraction were individually tabled and the combined gravity concentrate was ground in a ball mill to minus 75 μm. The ground concentrate was combined with the original minus 75-μm fraction and deslimed at 10 μm. The final flotation concentrate recovered 34 pct of the TiO_2 in a 54.8-pct-TiO_2 concentrate.

Comparison of Flotation Methods

To compare the efficiency of the flotation methods, consideration must be given to both reagent consumption and rutile grade and recovery. A summary of the reagent requirements for each method is shown in table 8. These data show that significant savings in reagent consumption can be made by lowering the amount of material sent to flotation.

A summary of the results from the beneficiation schemes tested is shown in table 9. Several physical characteristics of the TiO_2 found in the tailings can be determined by comparing these results. For each method, the rutile in the flotation feed was never liberated. About 31 pct of the TiO_2 was liberated and recovered in the as-received minus 75- plus 10-μm fraction. Only 4 pct of the rutile was recovered from the ground

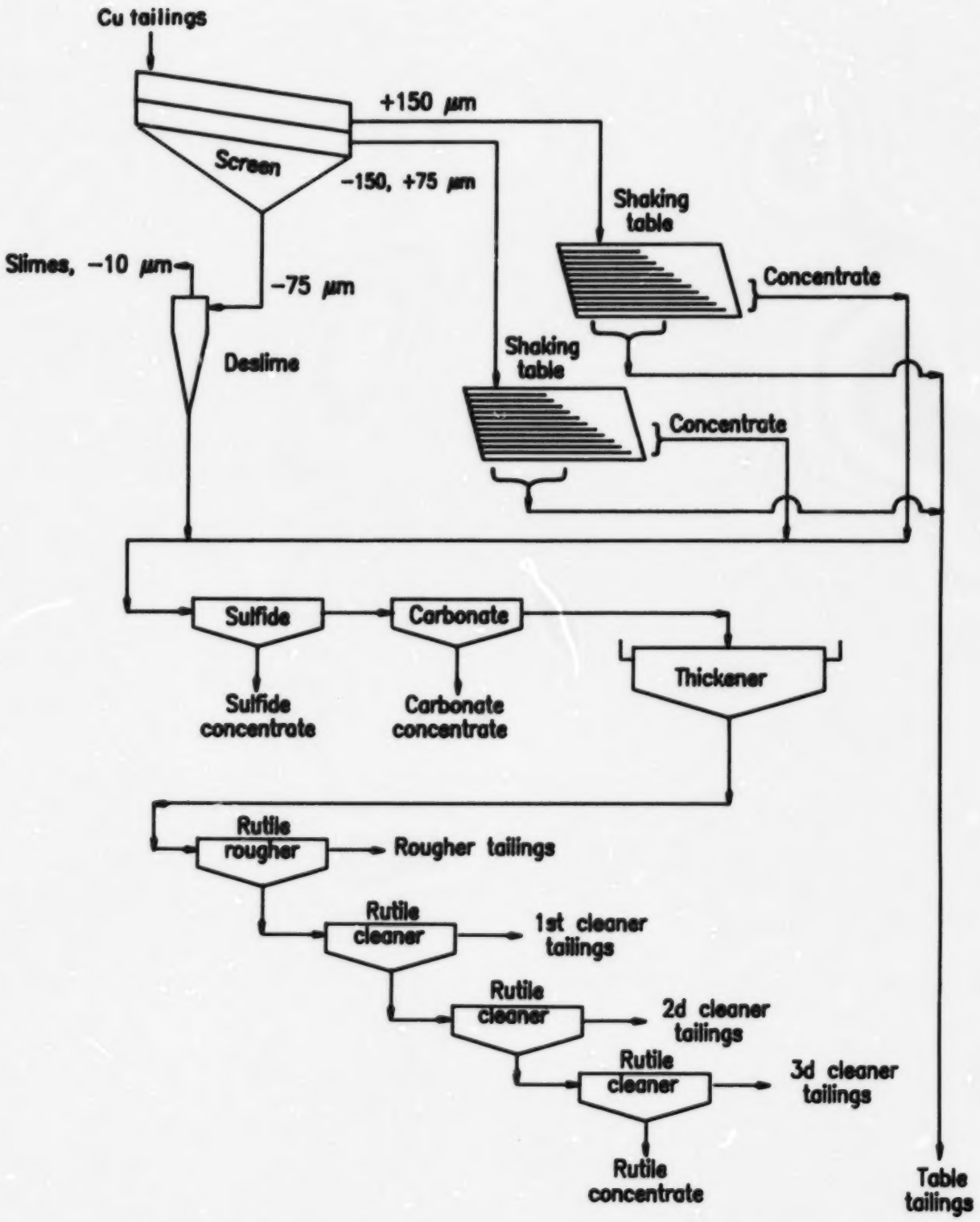

FIGURE 4.—Flow diagram, second alternate to Llewellyn and Sullivan method for rutile recovery.

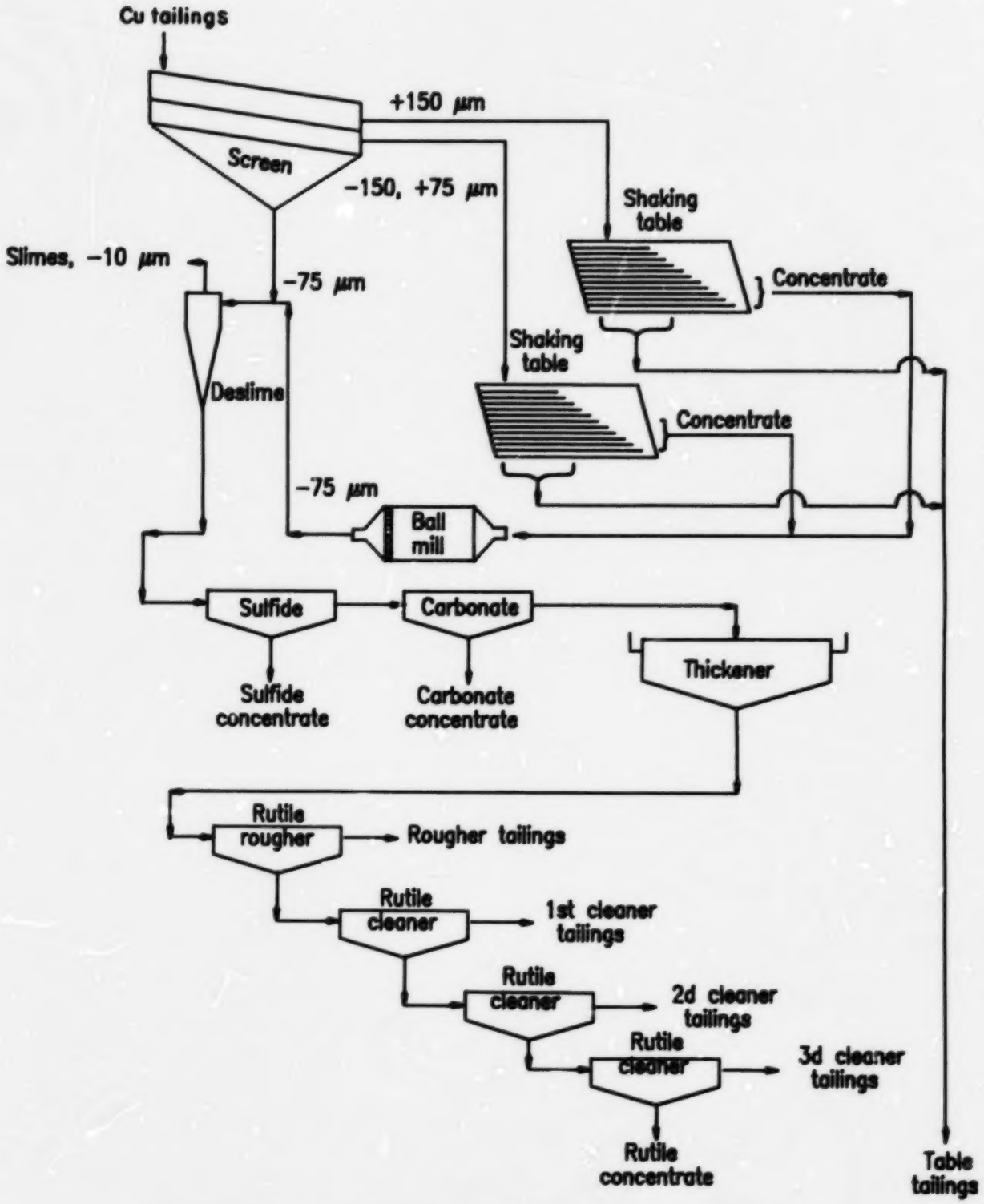

FIGURE 5.—Flow diagram, third alternate to Llewellyn and Sullivan method for rutile recovery.

TABLE 8. - Reagent schedule for sulfide, carbonate, and rutile flotation for the four recovery methods studied, pounds per short ton of original tailings.

Flotation method[1]	Sulfide flotation		Carbonate flotation		Rougher rutile flotation			Rutile cleaners (HF)
	NEX[2]	Frother	Sodium oleate	Dextrin	H_2SO_4	HF	Rutile collector	
Llewellyn and Sullivan.....	0.08	0.10	0.17	0.25	3.3	0.42	0.08	0.075
First alternate..	.02	.01	.02	.03	2.2	.06	.11	.03
Second alternate.	.04	.01	.04	.06	4.4	.09	.4	.04
Third alternate..	.02	.014	.02	.034	2.7	.06	.13	.034

[1]Differences are explained in the text and figures 3-5. [2]Sodium ethyl xanthate.

TABLE 9. - Comparison of results using the four rutile recovery methods, percent TiO_2

Flotation method	Rutile concentrate	TiO_2 recovery
Llewellyn and Sullivan.	34.7	31
First alternate.....	55.7	30
Second alternate.....	30.2	[1]24
Third alternate.....	54.8	34

[1]Over 30 pct of the rutile was recovered in the rougher flotation. Subsequent cleaner flotations lost significant amounts of rutile.

gravity concentrate. Although 32 pct of the TiO_2 was in the plus 75-µm portion of the tailings, at most only 4 pct was recovered by any of the three alternative methods. This information coupled with the heavy-liquid analysis showed that only 34 pct of the TiO_2 was liberated and recoverable in tailings sample 1B. Even at this low recovery potential, the quantity of recoverable rutile being discarded annually at the mill that supplied this sample approaches 18 pct of U.S. domestic rutile consumption.

OTHER BYPRODUCT ELEMENTS RECOVERY

Several other important elements and minerals were discovered in the Cu tailings samples studied. In several cases, beneficiation techniques were utilized to concentrate these elements and minerals so their modes of occurrence could be further characterized. Tungsten values in the samples ranged from trace amounts to 0.38 lb/st. Scheelite was identified as the primary W mineral. Beneficiation tests were conducted on the sample with the highest W values. After screening the tailings sample at 150, 75, and 37 µm, and desliming at 10 µm each size fraction was tabled to concentrate the heavy minerals. The sulfide minerals were removed from the table concentrates by flotation. Finally, the nonmagnetic

W concentrate was separated from the magnetic sulfide flotation tailings on a high-intensity wet magnetic separator. A W concentrate analyzing 2.4 pct WO_3 was produced by this treatment with about 87 pct recovery of the WO_3. A small portion of the scheelite was finer than 10-μm size and was not readily recovered by this method.

In nine of the eleven samples, Co ranged from 0.02 to 0.18 lb/st. From 7 to 25 pct of the Co was concentrated in the sink 3.3 sp gr fraction by heavy-liquid separation. The sulfide flotation concentrate from sample 1B contained 1.2 lb/st Co, which was 30 pct of the Co in the sample. Although no specific Co mineral was identified, microprobe analysis indicated that about one-fifth of the pyrite grains contained Co. There was little hope for improved Co concentration by physical beneficiation techniques. A preliminary test utilizing amminoacal leaching of oxidized sulfide concentrate followed by ion-exchange treatment showed that the Co could be extracted from the Cu tailings. This test recovered 15 pct of the Co from the tailings sample 1B. At 20 million st annual capacity from this mine, over 300,000 lb of Co could be recovered by this method. This represents 2 pct of U.S. domestic consumption (10) of this important element.

ACID LEACHING

The head samples and the minus 10-μm fractions of 10 of the porphyry Cu tailings were leached with H_2SO_4 to determine the solubility of various elements. Sample 11 was not received in time to be included in this study. Twenty-five-gram samples were leached for 4 h on a steam bath using 50 mL of 25 pct H_2SO_4. The leached samples were filtered and washed five times with hot distilled water. Leach and wash solutions were combined and analyzed for 20 elements by plasma spectrometry techniques. Arsenic, boron, and antimony were not detected in any of the leach solutions. Results for the remaining 17 elements are shown in table 10.

All solutions analyzed represented a 10:1 dilution of the original 50-mL leach solution. Analyses of the leach solutions from the minus 10-μm fractions for Al and P were omitted because significant quantities of tetrasodium pyrophosphate as a dispersant and $Al_2(SO_4)_3$ as a flocculant were used to obtain these slimes. These soluble salts may remain with the dried solids and report in the leach solution, giving erroneous results.

The Bureau chemists who performed the plasma spectrometry analyses (table 10) cautioned that spectral and background interferences create uncertainty about the presence of elements in the lower concentration ranges, particularly below about 0.01 g/L. Aluminum and calcium, for example, give major interference with W and U, respectively, and small errors in the programmed correction factors can give a false indication of the presence of these elements.

TABLE 10. - Plasma spectrometry analyses of leach solutions, grams per liter[1]

Sample	Product leached	Al	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn
1A.....	Heads....	0.26	0.34	ND	ND	0.0008	0.037	0.44	0.23	0.075
	Slimes...	([2])	.35	ND	0.0006	.002	.077	.69	.30	.008
2.....	Heads....	.22	.69	ND	ND	.0008	.030	.45	.13	.004
	Slimes...	([2])	.30	ND	ND	.004	.030	1.69	.19	.004
3.....	Heads....	.28	.44	ND	ND	ND	.03	.52	.23	.016
	Slimes...	([2])	.38	ND	ND	.0007	.008	.77	.33	.020
4.....	Heads....	.17	.34	ND	ND	ND	.084	.38	.20	.016
	Slimes...	([2])	.28	0.0008	.007	.0008	.073	2.21	.36	.087
5.....	Heads....	.233	.52	ND	ND	ND	.012	2.63	.25	.12
	Slimes...	([2])	.45	.0007	.001	.0007	.065	2.01	.30	.079
6.....	Heads....	.233	.55	ND	ND	ND	.006	.40	.40	.017
	Slimes...	([2])	.47	ND	ND	ND	.012	.57	.60	.021
7A.....	Heads....	.350	.53	.0008	ND	.0008	.11	1.86	.53	.021
	Slimes...	([2])	.43	.001	ND	.001	.16	2.65	1.00	.029
7B.....	Heads....	.278	.48	.0007	ND	.0007	.056	1.71	.37	.077
	Slimes...	([2])	.36	.001	ND	.001	.16	2.60	1.18	.12
8.....	Heads....	.234	.45	ND	ND	ND	.015	.31	.42	.027
	Slimes...	([2])	.48	ND	ND	ND	.042	.56	.69	.045
9A.....	Heads....	.120	.10	ND	ND	ND	.011	.21	.06	.005
	Slimes...	([2])	.16	ND	ND	ND	.029	.37	.11	.008
9B.....	Heads....	.120	.09	ND	ND	ND	.008	.19	.61	.005
	Slimes...	([2])	.011	ND	ND	ND	.049	1.01	.09	.002
10.....	Heads....	.413	.46	ND	ND	.001	.012	.49	.48	.007
	Slimes...	([2])	.31	ND	ND	.003	.033	.73	.68	.006

Sample	Product leached	Mo	Ni	P	Pb	U	V	W	Zn
1A.....	Heads....	ND	0.002	0.050	0.0008	ND	ND	0.009	0.004
	Slimes...	0.0006	.004	([3])	.006	ND	ND	.013	.003
2.....	Heads....	.002	ND	.015	ND	0.002	ND	.008	.0008
	Slimes...	.004	.001	([3])	.0007	.002	0.002	.019	.002
3.....	Heads....	.0007	.0007	.029	.0007	.006	.001	.001	.0007
	Slimes...	.0007	.0007	([3])	.0007	.006	.001	.021	.001
4.....	Heads....	.0007	.0007	.015	.0007	.006	ND	.007	.015
	Slimes...	.002	.002	([3])	.001	.006	ND	.024	.060
5.....	Heads....	ND	ND	.029	ND	ND	ND	.018	.046
	Slimes...	.001	.001	([3])	.001	ND	ND	.022	.043
6.....	Heads....	.0009	.006	.021	.015	.009	.0009	.012	.004
	Slimes...	ND	ND	([3])	ND	ND	ND	.021	ND
7A.....	Heads....	.009	.0008	.24	.002	.006	.002	.031	.030
	Slimes...	.012	.0007	([3])	.002	.006	.003	.047	.055
7B.....	Heads....	.002	.0007	.12	.001	.005	.0007	.027	.047
	Slimes...	.002	.0007	([3])	.002	.004	.001	.042	.12
8.....	Heads....	ND	ND	.025	ND	.005	.0007	.010	.005
	Slimes...	.008	ND	([3])	ND	.006	.0007	.017	.008
9A.....	Heads....	ND	ND	.017	ND	.002	ND	.004	.002
	Slimes...	ND	ND	([3])	ND	.004	.0008	.011	.005
9B.....	Heads....	ND	ND	.017	ND	.002	ND	.004	.005
	Slimes...	ND	ND	([3])	ND	.001	ND	.014	.0007
10.....	Heads....	ND	.001	.063	ND	.005	ND	.011	ND
	Slimes...	ND	.002	([3])	ND	.005	ND	.021	.001

ND Not determined.

[1]Multiply values by 40 to obtain pounds of material leached per ton of solids.

[2]$Al_2(SO_4)_3$ used as flocculant during sizing caused error in analysis.

[3]Tetra-sodium phrophosphate used as dispersant during sizing caused error in analysis.

CONCLUSIONS

Among the Cu tailings samples investigated, nine contained more than 2.0 lb/st TiO_2 as rutile. Only about 9 to 44 pct of this rutile was liberated. Flotation of the minus 75- plus 10-μm material from one sample recovered 30 pct of the TiO_2 in a 55.7-pct-TiO_2 concentrate.

Tungsten was found at levels as high as 0.4 lb/st in some tailings samples. Scheelite was identified as the principal W mineral. Gravity concentration, flotation, and magnetic separation of the sample W values significantly concentrated the plus 10-μm scheelite to 2.4 pct WO_3 with 87 pct WO_3 recovery. Cobalt in 9 of the 11 tailings samples ranged from 0.02 to 0.18 lb/st. Sulfide flotation, oxidation roasting, ammoniacal leaching, and ion exchange recovered about 15 pct of the Co in a Co-rich solution.

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